SHORT PAPER

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A novel synthesis of selenosulfides from diselenides by samarium diiodide†

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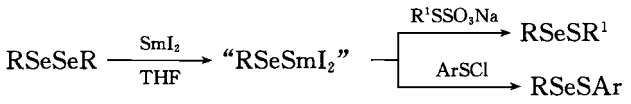
Diselenides were reduced by samarium diiodide in tetrahydrofuran (THF) to produce samarium selenolate. This selenolate anion reacted smoothly with sodium alkyl thiosulfates and phenylsulfenyl chloride to give selenosulfides in moderate to good yields.

Selenosulfides are useful intermediates of organic synthesis.[1] Several methods for the synthesis of selenosulfides have been reported, such as the reaction of thiols and selenols;[2] by heating the selenocyanate with thiols;[3] by refluxing a mixture of the diselenide and disulfide[4] or by the selenium transfer reagents,[5] *etc*.

Samarium diiodide (SmI_2) is of current interest in organic synthesis.[6] The utilization of SmI_2 in organic synthesis has been extensively documented, such as in the deoxygenation of sulfoxides[7] and epoxides,[8] the reduction of organohalo compounds,[9] the homocoupling allylic or benzylic halides,[10] acid chlorides,[11] carbonyl compounds,[12] the Barbier reaction,[13] and the Reformatsky reaction,[14] *etc*. Fukuzawa has reported that diselenide can be reductively cleaved into "$RSeSmI_2$" by samarium diiode for the synthesis of asymmetrical selenides.[15] Herein we wish to report the synthesis of selenosulfides using SmI_2. Some results are listed in Table 1.



Scheme 1

Table 1 The synthesis of selenosulfides by SmI_2

Entry	R	R^1	Ar	Yield (%)[a]
1	C_6H_5	*n*-C_4H_9		75
2	C_6H_5	*n*-C_6H_{13}		71
3	C_6H_5	*n*-C_8H_{17}		79
4	C_6H_5	$C_6H_5CH_2$		76
5	$C_6H_5CH_2$	*n*-C_4H_9		62
6	$C_6H_5CH_2$	*n*-C_6H_{13}		55
7	$C_6H_5CH_2$	*n*-C_7H_{15}		56
8	*p*-$CH_3C_6H_4$	*n*-C_6H_{13}		65
9	*n*C_4H_9	$C_6H_5CH_2$		52
10	C_6H_5		C_6H_5	76
11	*n*-C_4H_9		C_6H_5	60

[a]isolated yield.

The synthesis of S–Se bonded compounds by the reaction of the diselenide and sodium alkyl thiosulfate is recommended because of its simplicity and its mild condition. In our experiment work, it was found that diselenide reacts with 2 equivalents of SmI_2 at room temperature (R = phenyl, benzyl group), but when R is an alkyl group, it needs to be heated at 50–60 °C and then the blue-green color of samarium diiodide turned into yellow. A similar procedure can be carried out via phenylsulfenyl chloride.

The present methods provide a new path for the synthesis of compounds containing Se–S bonds. Moreover, it has advantages of mild conditions, simple operation and moderate to good yields.

Experimental

The solvent tetrahydronfuran (THF) was freshly distilled from sodium/benzophenone ketyl before its use. HMPA was dried by CaH_2 and was then distilled *in vacuo*. ^{1}H NMR spectra were recorded with a Bruker AC-80 spectrometer, using TMS as internal standard. IR spectra were determined on a PE-683 spectrometer. Mass spectra were determined on an HP 5989B instrument. Diselenide,[16] sodium alkyl thiosulfate[17] and phenyulsulfenyl chloride[18] were prepared by known methods.

General procedure for the synthesis of selenosulfides: Samarium power (0.15 g, 1 mmol), iodine (0.25 g, 1 mmol) and THF (10 ml) were mixed under a dinitrogen atmosphere, the mixture was stirred at 40 °C for 3h. A deep blue solution was obtained and cooled to room temperature. Diselenide (0.5 mmol) in 1 ml THF was added to the deep blue solution in one portion. The mixture turned yellow after 4h and sodium alkyl thiosulfate (1 mmol) was added. The reaction mixture was stirred for 4h. Dilute hydrochloric acid (2N, 5 ml) and ether (20 ml) were added. The organic layer was separated and the aqueous layer was extracted with ether (20 ml × 2). The combined organic layer was washed with saturated sodium thiosulfate, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel (cyclohexane as eluent).

A similar method can be carried out via phenylsulfenyl chloride. The procedure is same as the above method, sodium alkyl thiosulfate is replaced with the solution of PhSC1 (1 mmol) in 3 ml dry benzene.

1. *n*-C_4H_9SSePh light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.87 (t, 3H), 1.10–1.66 (m, 4H), 2.26–2.60 (t, 2H), 7.03–7.55 (m, 5H), IR ν_{max}/cm^{-1} : 3040, 2990, 1590, 1480, 1440, 1380, 1020, 1000, 730, 680, *m/z* (M^+, ^{80}Se) 246.

2. *n*-$C_6H_{13}SSePh$ light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.85 (t, 3H), 1.06–1.50 (m, 8H), 2.40–2.95 (t, 2H), 7.06–7.66 (m, 5H), IR ν_{max}/cm^{-1} : 3040, 2995, 1580, 1470, 1435, 1380, 1020, 740, 680, *m/z* (M^+, ^{80}Se) 274.

3. *n*-$C_8H_{17}SSePh$ light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.87 (t, 3H), 1.06–1.66 (m, 12H), 2.40–2.85 (t, 2H), 7.09–7.56 (m, 5H), IR ν_{max}/cm^{-1} : 3040, 2995, 1580, 1470, 1435, 1380, 1010, 750, 670, *m/z* (M^+, ^{80}Se) 302.

4. C_6H_5SSePh light yellow crystal, m.p. 36–38 °C ^{1}H NMR (CCl_4, δ_H) : 3.97 (s, 2H), 7.10–7.63 (m, 10H), IR ν_{max}/cm^{-1} : 3040, 3020, 2930, 2940, 1510, 1470, 690, *m/z* (M^+, ^{80}Se) 280.

5. *n*-$C_4H_9SSeCH_2Ph$ light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.85 (t, 3H), 1.06–1.70 (m, 4H), 2.27–2.60 (t, 2H), 3.90 (s, 2H), 7.03–7.55 (m, 5H), IR ν_{max}/cm^{-1} : 3040, 3020, 2970, 2935, 1660, 1505, 1460, 1385, 1170, 1060, 1035, 710, 690, *m/z* (M^+, ^{80}Se) 260.

6. *n*-$C_6H_{13}SSeCH_2Ph$ light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.87 (t, 3H), 1.10–1.80 (m, 8H), 2.27–2.70 (t, 2H), 3.96 (s, 2H), 7.03–7.55 (m, 5H), IR ν_{max}/cm^{-1} : 3040, 3020, 2975, 2940, 1510, 1385, 1180, 1020, 980, 760, 690, *m/z* (M^+, ^{80}Se) 288.

7. *n*-$C_7H_{15}SSeCH_2Ph$ light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.85 (t, 3H), 1.06–1.70 (m, 10H), 2.27–2.65 (t, 2H), 3.97 (s, 2H), 7.03–7.55 (m, 5H), IR ν_{max}/cm^{-1} : 2940, 2920, 2970, 2935, 1510, 1380, 1175, 1020, 980, 760, 690, *m/z* (M^+, ^{80}Se) 302.

8. *n*-$C_6H_{13}SSeC_6H_4$-CH_3(p) light yellow oil, ^{1}H NMR (CCl_4, δ_H) : 0.85 (t, 3H), 1.03–1.56 (m, 8H), 2.29 (s, 3H), 2.50–2.95 (t, 2H),

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

6.85–7.50 (m, 4H), IR ν_{max}/cm^{-1} ; 3045, 3020, 2970, 1600, 1495, 1460, 1380, 1310, 1180, 1160, 1020, 800, 720, *m/z* (M^+, ^{80}Se) 288.

9. $C_6H_5CH_2SSeC_4H_9$-(*n*) light yellow oil, ^1H NMR (CCl_4, δ_H) : 0.90 (t, 3H), 1.16–1.72 (m, 4H), 2.26–2.86 (t, 2H), 4.15 (s, 2H), 7.03–7.60 (m, 5H), IR ν_{max}/cm^{-1} ; 3040, 3020, 2980, 2940, 1510, 1465, 1380, 1170, 1070, 1035, 710, 690, *m/z* (M^+, ^{80}Se) 260.

10. $C_6H_5SeSC_6H_5$ m.p. 57–59 °C (Lit[19], 57–58 °C), ^1H NMR (CCl_4, δ_H) : 7.05–7.70 (m, 10H), IR ν_{max}/cm^{-1} ; 3040, 3020, 2940, 1520, 1470, 700.

11. *n*-$C_4H_9SeSC_6H_5$ light yellow oil, ^1H NMR (CCl_4, ppm), δ 1.00–1.61 (m, 4H), 2.21–2.57 (t, 2H), 7.15–7.80 (m, 5H); IR (ν_{max}/cm^{-1}) : 3030, 2990, 1590, 1480, 1440, 1380, 1020, 1005, 730, *m/z* (M^+, ^{80}Se) 246.

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